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**FINAL REPORT**

for

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**PHOTODISSOCIATION STUDIES OF SULFUR OXIDES**

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<p>The detailed reaction dynamics of several gas phase polyatomic systems has been established in this research at the Department of Chemistry at the University of Puerto Rico. Real time dynamics of sulfur monoxide photoelimination reactions have been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the <math>B^3\Sigma^+ - X^3\Sigma^-</math> transition in the region of 237-310 nm. The following group of molecules has been studied: Sulfur dioxide (<math>\text{SO}_2</math>), the thionyl halides (<math>\text{SOX}_2</math>; where X=F,Cl or Br), dimethyl sulfoxide (<math>(\text{CH}_3)_2\text{SO}</math>), ethylene episulfoxide (<math>(\text{CH}_2)_2\text{SO}</math>), trimethylene sulfoxide (<math>(\text{CH}_2)_3\text{SO}</math>), tetramethylene sulfoxide (<math>(\text{CH}_2)_4\text{SO}</math>), and thionyl aniline (<math>\text{C}_6\text{H}_5\text{NSO}</math>). In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. A broad picture of sulfur monoxide photoelimination reactions emerges from this work. In a second area, the photophysics and photochemistry of the vinoxy radical were investigated. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, HCl, CO<sub>2</sub>, N<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, SF<sub>6</sub> and CH<sub>3</sub>OCH=CH<sub>2</sub>. The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å<sup>2</sup>. A vibrational level dependence was found for the radiative lifetimes. A kinetic model, consistent with all the experimental observations has been postulated. Several new transitions of the CH<sub>2</sub>CHO (B-X) transition have been discovered. Finally, a study of bimolecular reactions has been initiated.</p> <p>One of the primary goals of this grant was to provide funding to a Ph.D. candidate. The first three years of the doctoral work of Ms. Katherine I. Barnhard de Sanfiorenzo was supported for with this grant. Ms. Barnhard de Sanfiorenzo will finish her doctoral work by the end of 1996. In addition, the grant stimulated a wider degree of interest in our research group on the photodissociation dynamics of polyatomic molecules.</p>			
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## ABSTRACT

The detailed reaction dynamics of several gas phase polyatomic systems has been established in this research at the Department of Chemistry at the University of Puerto Rico. Real time dynamics of sulfur monoxide photoelimination reactions have been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the  $B^3\Sigma^+ - X^3\Sigma^+$  transition in the region of 237-310 nm. The following group of molecules has been studied: Sulfur dioxide  $\{SO_2\}$ , the thionyl halides  $\{SOX_2\}$ , where  $X=F, Cl$  or  $Br$ , dimethyl sulfoxide  $\{(CH_3)_2SO\}$ , ethylene episulfoxide  $\{(CH_2)_2SO\}$ , trimethylene sulfoxide  $\{(CH_2)_3SO\}$ , tetramethylene sulfoxide  $\{(CH_2)_4SO\}$ , and thionyl aniline  $\{C_6H_5NSO\}$ . In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. A broad picture of sulfur monoxide photoelimination reactions emerges from this work. In a second area, the photophysics and photochemistry of the vinoxy radical were investigated. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, HCl, CO<sub>2</sub>, N<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, SF<sub>6</sub> and CH<sub>3</sub>OCH=CH<sub>2</sub>. The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å<sup>2</sup>. A vibrational level dependence was found for the radiative lifetimes. A kinetic model, consistent with all the experimental observations has been postulated. Several new transitions of the CH<sub>2</sub>CHO (B-X) transition have been discovered. Finally, a study of bimolecular reactions has been initiated.

One of the primary goals of this grant was to provide funding to a Ph.D. candidate. The first three years of the doctoral work of Ms. Katherine I. Barnhard de Sanfiorenzo was supported for with this grant. Ms. Barnhard de Sanfiorenzo will finish her doctoral work by the end of 1996. In addition, the grant stimulated a wider degree of interest in our research group on the photodissociation dynamics of polyatomic molecules.

## I. OBJECTIVES OF THE RESEARCH EFFORT

The objectives of this research effort were:

- (1) To provide funding for a Ph.D. candidate at a minority institution for research in photochemistry and molecular dynamics using state-of-the-art laser techniques in conjunction with the AFOSR grants: *Photodissociation Studies of Polyatomic Free Radicals* (F49620-89-C-0070) and *Photofragmentation Spectroscopy and Photodissociation Dynamics of Polyatomic Molecules* (F49620-93-1-0110).
- (2) The development of an experimental program in gas phase photochemistry and unimolecular dissociation dynamics of polyatomic species.
- (3) To provide a more detailed understanding of the unimolecular dissociation dynamics of sulfur oxides, such as,  $\text{SO}_2$ ,  $\text{Br}_2\text{SO}$ ,  $\text{Cl}_2\text{SO}$ , and  $(\text{CH}_3)_2\text{SO}$ .
- (4) To extend the established methods of photodissociation dynamics for closed shell species to open-shell species.

## II. ACCOMPLISHMENTS OF THE RESEARCH EFFORT

This research effort was initiated August 15, 1992, and we believe that the project has reached or at least made significant advances towards the stated goals. The project was in conjunction with two other grants with the Air Force Office of Scientific Research: *Photodissociation Studies of Polyatomic Free Radicals* (Contract Number F49620-89-C-0070), and *Photofragmentation Spectroscopy and Photodissociation Dynamics of Polyatomic Molecules* (F49620-93-1-0110). During the course of the contract, numerous accomplishments and goals have been achieved and reported. Now at the end of 3 years (the term of the contract), we report on the extent of the accomplishments, and how well these results met the stated objectives

In developing our program in gas phase photochemical dynamics of polyatomic molecules, we have done (and continue to do) a body of experimental studies on sulfur monoxide ( $\text{SO}$ ) photoelimination reactions. This work was motivated by the importance of sulfur oxides in atmospheric and combustion environments, and was co-supported by a second AFOSR award. The following group of molecules has been studied: Sulfur dioxide  $\{\text{SO}_2\}$ , the thionyl halides  $\{\text{SOX}_2\}$ ,

where  $X=F, Cl$  or  $Br\}$ , dimethyl sulfoxide  $\{(CH_3)_2SO\}$ , ethylene episulfoxide  $\{(CH_2)_2SO\}$ , trimethylene sulfoxide  $\{(CH_2)_3SO\}$ , tetramethylene sulfoxide  $\{(CH_2)_4SO\}$ , and thionyl aniline  $\{C_6H_5NSO\}$ . In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. What follows is a brief description of the results found for each of these molecular systems.

## II.1. $SO_2$

Due to the large number of studies on the 193 nm photodissociation of sulfur dioxide, we used this system primarily as a test of our laser induced fluorescence (LIF) technique. Our work, however, led us to some interesting discoveries and discrepancies with past work on the 193 nm photodissociation of  $SO_2$ . We therefore embarked on a reinvestigation of the photodissociation dynamics of  $SO_2$ . We have measured the nascent vibrational, rotational, and spin-state distributions of the  $SO(X^3\Sigma)$  fragment in both a bulb and in a pulsed supersonic nozzle following 193 and 210 nm irradiation of  $SO_2$ . The 210 nm laser light was obtained by Raman shifting the ArF excimer laser transition to the first Stokes line in hydrogen gas. Our vibrational distribution following 193 nm photolysis was consistent with past measurements (not by LIF), giving us confidence in our experimental methods. The SO vibrational distribution at 210 nm is found to peak at  $v''=1$ . We do find differences in the rotational state distributions obtained in the bulb vs. free jet experiments, which is surprising for the predissociative nature of sulfur dioxide. We have also discovered an interesting spin polarization effect in the nascent SO photofragment, that varies with vibrational level, and appears to have a strong  $J$  dependence. The bimodal rotational distributions have been modelled using our kinematic distribution model (see below), and suggest that there are two crossing points for the predissociation of  $SO_2$ . These more detailed results on the photodissociation of  $SO_2$  are being prepared for publication in the *Journal of Chemical Physics*.

## II.2. $Cl_2SO$

Due to our extremely sensitive and quantum specific capabilities for the detection of  $SO(X^3\Sigma)$ , we have studied the photodissociation dynamics of thionyl halides. The photodissociation of thionyl chloride ( $Cl_2SO$ ) is of interest as a model system to study three-body fragmentation

processes, which can occur either in concert or stepwise. The photodissociation of this tetratomic molecule at 193 and 248 nm has been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the  $B^3\Sigma^+ - X^3\Sigma^+$  transition in the region of 237-295 nm. Photolysis of  $Cl_2SO$  at 193 nm leads to an inverted vibrational distribution for the nascent  $SO(X^3\Sigma^+)$  with a population maximum at  $v''=2$ . The quantum yield,  $\Phi_{SO(X)}^{193\text{ nm}} = 0.73 \pm 0.10$ , has been measured by comparison of the  $SO(X^3\Sigma^+)$  produced from  $SO_2$ . The results indicate a concerted three-body fragmentation mechanism as the primary dissociation channel. A Franck-Condon/golden rule model elucidates the geometry prior to the fragmentation and suggests a direct dissociation mechanism. The rotational and spin state distributions have been measured from the rovibronically resolved spectra to support our model of the detailed dissociation mechanism. At 248 nm, the nascent vibrational distribution was found to be bimodal. The vibrational state population distribution in  $v''=0-2$ , which accounts for most (~94%) of the nascent  $SO(X^3\Sigma^+)$  population, was found to be thermal ( $T_{vib}=1000 \pm 200K$ ), suggesting a stepwise fragmentation process. About 6% of the nascent SO population has been observed in other vibrational levels ( $v''=3-7$ ), and most likely originates from the molecular elimination of  $Cl_2$  from  $Cl_2SO$ .

These results provide important evidence of wavelength dependent photolysis channels in polyatomic molecules, and go further in characterizing them in microscopic detail. The original premise of  $Cl_2SO$  being a good model for polyatomic photodissociation dynamics studies is borne out. This work was published in the *Journal of Physical Chemistry* (J. Phys. Chem. 97, 1993, 12260).

### II.3. $F_2SO$

The vibrational and rotational state distributions and the primary quantum yield of the  $SO(X^3\Sigma^+)$  fragment following the laser photolysis of  $F_2SO$  at 193 nm have been measured by using laser induced fluorescence spectroscopy on the  $SO(B^3\Sigma^+ - X^3\Sigma^+)$  transition. Molecular elimination of  $F_2$  is the only energetically-allowed channel to produce the SO fragment. The quantum yield measurement,  $\Phi_{SO(X)}^{193\text{ nm}} = 0.06 \pm 0.01$ , suggests that other photochemical channels, *i.e.*,  $FSO + F$ , must be operative as well. The vibrational distribution of the nascent  $SO(X)$  fragment has been found to be inverted with a population maximum at  $v'' = 2$ , indicating a rapid dissociation process, and suggests that the nascent  $F_2$  fragment is born with significant vibrational excitation. A Franck-Condon model best fits the observed vibrational state distribution when the SO bond length is similar to that of the ground state  $F_2SO$ . For more details on this work, see the full publication in *Chemical*

*Physics Letters* (Chem. Phys. Lett. 216, 1993, 537).

In our attempts to fully understand the photochemistry of  $\text{F}_2\text{SO}$ , we are seeking other ways to detect FSO radical. This involves both experiment and theory. The structure and spectroscopic properties of the ground  $^2\text{A}^{\prime\prime}$  state of FSO and its isomer, FOS, have been determined at the single and double excitation quadratic configuration interaction level of theory with a 6-311G(2d,f) Gaussian basis set. The local minimum corresponding to the isomer FOS lies about 84 kcal/mol above the global minimum structure corresponding to the FSO radical. A number of single-point QCISD calculations were performed with a small 6-311G\* basis set to obtain qualitative features of the conformational potential energy surface for the isomerization FSO  $\rightarrow$  FOS. Optimized geometries obtained for FSO are in excellent agreement with microwave spectroscopy data. A search for the electronic states of FSO is currently underway in our laboratory. The calculated results can be found in greater detail in an upcoming publication in the *Journal of Molecular Structure* (accepted).

#### II.4. $\text{Br}_2\text{SO}$

Photodissociation of  $\text{Br}_2\text{SO}$  following irradiation at 193 and 248 nm has been studied by laser induced fluorescence spectroscopy of the nascent SO fragment. The vibrational distributions for the nascent SO have been found to be inverted, suggesting a concerted mechanism for the dissociation at both wavelengths. A Franck Condon / Golden Rule model elucidates the geometry prior to the dissociation, suggesting the possibility that photodissociation at both wavelengths occurs via the same excited state of  $\text{Br}_2\text{SO}$ . The rotational and spin state distributions have been measured from rovibronically resolved spectra to support our discussion on the detailed dissociation mechanism. Quantum yield measurements suggest that other electronic states of the SO radical may be directly produced. This work will be published in *Chemical Physics Letters*.

#### II.5. $(\text{CH}_3)_2\text{SO}$

The photodissociation dynamics of the reaction,  $(\text{CH}_3)_2\text{SO} + \text{hv}(193 \text{ nm}) \sim 2\text{CH}_3 + \text{SO}$ , have been examined by laser spectroscopic techniques. Relative vibrational and rotational state energy distributions of the nascent SO photofragment have been determined by using laser induced fluorescence spectroscopy on the ( $\text{B}^3\Sigma^+ - \text{X}^3\Sigma^+$ ) transition. The same technique has also been employed to establish the quantum yield,  $\Phi_{193}[\text{SO}(\text{X}^3\Sigma)] = 1.02 \pm 0.12$ . The nascent vibrational state

distributions in the  $\nu_1$  and  $\nu_2$  modes of the methyl radical have been determined by using 2+1 resonance enhanced multiphoton ionization spectroscopy via the  $(3p\ ^2A_2'' \sim 2p\ ^2A_2'')$  transition. These measurements were done in collaboration with M. Hawley and H.H. Nelson at the Naval Research Laboratory.

The energy distributions of the nascent fragments are best described by a concerted three-body fragmentation. While some of our data are suggestive of a concerted synchronous dissociation of the two S-C bonds in DMSO, we cannot conclusively determine the synchronicity from our results. Further studies of the photofragment angular distributions following 193 nm irradiation of dimethyl sulfoxide would be helpful in analyzing this aspect of the dissociation dynamics. This work appeared in the *Journal of Physical Chemistry* (J. Phys. Chem. 97, 1993, 12269).

## II.6. $(CH_2)_2SO$

The photochemistry of ethylene episulfoxide,  $(CH_2)_2SO$ , has been investigated for the first time in our laboratory. Photodissociation of  $(CH_2)_2SO$  at 193 and 248 nm produces  $SO(v''=0-6)$  and  $SO(v''=0-5)$ , respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at  $v''=1$  in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent  $SO(X^3\Sigma)$  photofragment. These models are unable to fit the experimental observations, when the other fragment is ground state ethylene, but excellent correlation is obtained for the lowest energy triplet state of  $C_2H_4$ . The time-dependent behavior of the  $SO(X^3\Sigma)$  LIF signal has been measured, indicating a second ground state sulfur monoxide production pathway. The experimental  $SO(X^3\Sigma)$  transients can be fit by a biexponential function. The slower production of  $SO(X^3\Sigma)$  is believed to be due to relaxation of  $SO(a^1\Delta)$ , which is also produced in the photodissociation of  $(CH_2)_2SO$ . Quantum yields for the of  $SO(a^1\Delta)$  and  $SO(X^3\Sigma)$ , based on a kinetic analysis, are  $0.25 \pm 0.02$  and  $0.41 \pm 0.05$  following 193 nm irradiation of  $(CH_2)_2SO$ , and  $0.34 \pm 0.03$  and  $0.44 \pm 0.06$  for the 248 nm photolysis. A manuscript of this work will be submitted to the *Journal of the American Chemical Society* in the near future.

## II.7. $(\text{CH}_2)_3\text{SO}$

The photochemistry of trimethylene sulfoxide,  $(\text{CH}_2)_3\text{SO}$ , has been investigated in our laboratory. Photodissociation of  $(\text{CH}_2)_3\text{SO}$  at 193 and 248 nm produces  $\text{SO}(v''=0-6)$  and  $\text{SO}(v''=0-6)$ , respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at  $v''=1$  in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent  $\text{SO}(\text{X}^3\Sigma)$  photofragment. Both the Franck-Condon modelling of the vibrational state distributions and the impulsive modeling of the total internal energies of the photofragments, indicate that the photodissociation of trimethylene sulfoxide proceeds via a concerted fragmentation process to produce  $\text{SO}(\text{X}^3\Sigma)$  and a trimethylene diradical. The two products are decoupled before the stable hydrocarbons, found in earlier product studies, are formed. The similar fragmentation products and the similar rotational temperatures in each vibrational level, as well as the similar inverted vibrational state distributions of the  $\text{SO}(\text{X}^3\Sigma)$  photofragments for both 193 and 248 nm photolyses suggest that the dissociation occurs on the same potential surface. Best fit bond lengths, however, of the dressed SO molecule in the Franck-Condon model are found to be different for the 193 and 248 nm cases. The impulsive model calculation revealed that the values of the out-of-plane angle of the transition state of the trimethylene sulfoxide are also different at the two photolysis wavelengths. This result indicates that the geometries of the transition states are different for the 193 and 248 nm photolyses of the trimethylene sulfoxide. The UV absorption spectrum of  $(\text{CH}_2)_3\text{SO}$  reveals that the 193 and 248 nm absorptions belong to different absorption bands. The dissociation most likely occurs on two different potential energy surfaces. This work is being prepared for submission in the *Journal of Physical Chemistry*.

## II.8. $(\text{CH}_2)_4\text{SO}$

The 193 and 248 nm photodissociation of tetramethylene sulfoxide (TMSO) in the gas phase has been investigated by the same laser spectroscopy techniques as described above, and the vibrational state distributions of the nascent  $\text{SO}(\text{X}^3\Sigma)$  photofragment have been measured at both wavelengths. These vibrational state distributions can be characterized as Boltzmann with vibrational temperatures of  $1250 \pm 60$  and  $1220 \pm 60$  K for the 193 and 248 nm photolyses respectively. Assuming that the SO photofragment is produced in concert with a 1,4-tetramethylene diradical, the

vibrational state distribution obtained in the 193 nm photolysis agrees well with an energy disposal model, in which the full reaction exoergicity is statistically partitioned among all the products' degrees of freedom. The quantum yield for  $\text{SO}(\text{X}^3\Sigma)$  production at 193 nm,  $\Phi_{\text{SO}(\text{X})}^{193\text{ nm}} = 0.47 \pm 0.20$ , has been obtained by comparison with  $\text{SO}_2$  photolysis. For the 248 nm photodissociation, the experimentally obtained vibrational state distribution can be best described by a variant statistical model assuming three-body fragmentation, i.e. the products are an SO fragment and two ethylene molecules. The quantum yield for  $\text{SO}(\text{X}^3\Sigma)$  production at 248 nm is  $\Phi_{\text{SO}(\text{X})}^{248\text{ nm}} = 0.44 \pm 0.19$ . The OH photofragment has been detected during both the 193 and 248 nm photolyses of TMSO. The rotational state distributions of the  $\text{OH}(\text{X}^2\Pi, v''=0)$  fragment have been determined by LIF spectroscopy using the A-X transition. The hydroxy rotational temperatures can be characterized as  $600 \pm 50$  and  $510 \pm 40$  K following photolysis of TMSO at 193 and 248 nm, respectively. The differences in the 193 and 248 nm photolyses can be explained if two different surfaces, i.e. a singlet and triplet, are advanced. For further details on this work, see the publication in the *Journal of Physical Chemistry* (J. Phys. Chem. 99, 1995, 17380).

## II.9. $\text{C}_6\text{H}_5\text{NSO}$

The photochemistry of thionyl aniline has been examined for the first time. Photodissociation of  $\text{C}_6\text{H}_5\text{NSO}$  at 193 and 248 nm produces  $\text{SO}(v''=0-5)$  and  $\text{SO}(v''=0-5)$ , respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at  $v''=1$  in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent  $\text{SO}(\text{X}^3\Sigma)$  photofragment. Both the Franck-Condon modelling of the vibrational state distributions and the impulsive modeling of the total internal energies of the photofragments, indicate that the photodissociation of trimethylene sulfoxide proceeds via a concerted fragmentation process to produce  $\text{SO}(\text{X}^3\Sigma)$  and a phenyl nitrene species. A new spectrum in the range of 440-520 nm has been recorded. While early speculations believed that this was due to the ground state triplet of phenyl nitrene, we now believe that the dehydroazepine species is the carrier of the spectrum. The dissociation is believed to produce SO and singlet phenyl nitrene, which undergoes ring expansion to the dehydroazepine. This work is being prepared for submission to the *Journal of the American Chemical Society*.

## II.10. $\text{C}_2\text{H}_3\text{O}$

State specific radiative lifetimes and electronic quenching cross-sections were measured for four different vibrational modes of  $\text{CH}_2\text{CHO}$  ( $\tilde{\text{B}}^2\text{A}''$ ). Ground state vinoxy radicals were produced by 193nm excimer laser photolysis of  $\text{CH}_3\text{OCH}=\text{CH}_2$ , and pumped to the  $\tilde{\text{B}}$  state by a tunable dye laser operating between 332 and 348nm. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, HCl, N<sub>2</sub>O, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>,  $\text{CH}_3\text{OCH}=\text{CH}_2$  and SF<sub>6</sub>. The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å<sup>2</sup>. Zero pressure radiative lifetimes are found to vary from 98±10 to 154±18 ns, depending on the vibrational mode. A resulting mechanism, consistent with all the observations, can be summarized into a kinetic model. For further details on the model, see the publication in the *Journal of Physical Chemistry* (J. Phys. Chem. 100, 1996, xxxx).

### III. PUBLICATIONS

15. Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner, "*The Laser Photochemistry of Thionylaniline*", manuscript in preparation.
14. Fei Wu, Xirong Chen, and Brad R. Weiner, "*Photodissociation Dynamics of Trimethylene Sulfoxide*", manuscript in preparation.
13. Ruolian Wan, Xirong Chen, Katherine I. Barnhard, and Brad R. Weiner, *Observation of New Vibrational modes of the CH<sub>2</sub>CHO Radical*", to be submitted to Chem. Phys. Lett.
12. Fei Wu, Xirong Chen and Brad R. Weiner, "*The Photochemistry of Ethylene Episulfoxide*", to be submitted to J. Am. Chem. Soc.
11. Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner, "*The 193 and 210 nm Photodissociation of Sulfur Dioxide*", to be submitted to J. Chem. Phys.
10. Hongxin Wang, Xirong Chen, Manuel A. Rivera and Brad R. Weiner, "*Photochemistry of Thionyl Bromide at 248 and 193 nm in the Gas Phase*", to be submitted to Chemical Physics
- 9.. Luis A. Muñoz, Brad R. Weiner and Yasuyuki Ishikawa, "*Conformational Potential Energy Surface of the FSO Radical and its Isomer FOS in the Ground <sup>2</sup>A" State*", J. Mol. Struct. **1996**, in press..
8. Katherine I. Barnhard, Min He and Brad R. Weiner, "*Excited State Dynamics of CH<sub>2</sub>CHO(B<sup>2</sup>A')*", J. Phys. Chem. **100**, **1996**, xxxx.
7. Fei Wu, Xirong Chen and Brad R. Weiner, "*Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm in the Gas Phase*", J. Phys. Chem. **99**, **1995**, 17380.
6. Fei Wu, Xirong Chen and Brad R. Weiner, "*Photodissociation Studies of Cyclic Sulfoxides*", SPIE Proceedings (Laser Techniques for State-Selected and State-to-State Chemistry III), **2548**, **1995**, 355.
5. Katherine I. Barnhard, Min He and Brad R. Weiner, "*Radiative Lifetimes and Electronic State Quenching of CH<sub>2</sub>CHO(B<sup>2</sup>A')*", SPIE Proceedings (Laser Techniques for State-Selected and State-to-State Chemistry III), **2548**, **1995**, 340.
4. Hongxin Wang, Xirong Chen and Brad R. Weiner, "*SO(X<sup>3</sup>Σ) Production from the 193 nm Laser Photolysis of Thionyl Fluoride*", Chem. Phys. Lett. **216**, **1993**, 537.
3. Xirong Chen, Hongxin Wang, Brad R. Weiner, Michael Hawley and H.H. Nelson, "*Photodissociation of Dimethyl Sulfoxide at 193 nm in the Gas Phase*", J. Phys. Chem. **97**, **1993**, 12269.

2. Hongxin Wang, Xirong Chen, and Brad R. Weiner, "Laser Photodissociation Dynamics of Thionyl Chloride: Concerted and Stepwise Cleavage of S-Cl Bonds", *J. Phys. Chem.* **97**, 1993, 12260.
1. Xiaotian Gu, Luis A. Muñoz, Yasuyuki Ishikawa, and Brad R. Weiner, "Isotope Effects and Wavelegth Dependence in the Rotational State Distributions of the Diatomic Photofragments, SH and SD, from the Photodissociation of H<sub>2</sub>S and D<sub>2</sub>S", *Chem. Phys. Lett.* **211**, 1993, 65.

#### **IV. PERSONNEL**

The following people have participated in this project in addition to the principal investigator.

##### **Graduate Students**

Katherine I. Barnhard de Sanfiorenzo(Department of Chemistry, Ph.D. expected August 1996)

## V. PRESENTATIONS

### International / National (14)

14. *"Photodissociation Dynamics of Cyclic Sulfoxides"*  
Fei Wu, Xirong Chen and Brad R. Weiner  
Third Pan American Chemical Congress, San Juan, Puerto Rico, September 10-15, 1995
13. *"Radiative Lifetimes and Electronic State Quenching of CH<sub>2</sub>CHO(B<sup>2</sup>A")"*  
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner  
Third Pan American Chemical Congress, San Juan, Puerto Rico, September 10-15, 1995
12. *"Photodissociation Dynamics of Cyclic Sulfoxides"*  
Fei Wu, Xirong Chen and Brad R. Weiner  
SPIE Laser Techniques for State-Selected and State-to-State Chemistry III, San Diego, California, July 1995
11. *"State-Resolved Fluorescence Quenching and Predissociation of the Vinoxy Radical: Evidence for Mode-Selective Bond-Scission"*  
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner  
SPIE Laser Techniques for State-Selected and State-to-State Chemistry III, San Diego, California, July 1995
10. *"The Laser Photchemistry of Thionylaniline"*  
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner  
50th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1995
9. *"The Laser Photchemistry of Thionylaniline"*  
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner  
209th National Meeting of the American Chemical Society, Anaheim, California, 2-7 April 1995.
8. *"State-Resolved Distributions of Nascent SO(X<sup>3</sup>Σ, v") following SO<sub>2</sub> Photodissociation"*  
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner  
10th Interdisciplinary Laser Science Conference, Dallas, Texas, 2-7 October 1994.
7. *"State-Resolved Predissociative Dynamics of the Vinoxy (CH<sub>2</sub>CHO) Radical"*  
Katherine I. Barnhard, Min He, Provi Mayo and Brad R. Weiner  
10th Interdisciplinary Laser Science Conference, Dallas, Texas, 2-7 October 1994.
6. *"Energy Disposal as a Probe of the Ultraviolet Photodissociation Dynamics of Sulfur Dioxide".*  
Fei Wu, Xirong Chen and Brad R. Weiner  
1994 Gordon Research Conference on Atomic and Molecular Interactions, New London,

New Hampshire, 3-8 July 1994

5. *"Photochemistry of N-substituted thionylimides".*  
Rubén Delgado, Karl Matos, Xirong Chen and Brad R. Weiner  
207th National Meeting of the American Chemical Society, San Diego, California, 13-17 March 1994.
4. *"Photochemistry of Thionyl Bromide at 193 and 248 nm in the Gas Phase"*  
Hongxin Wang, Xirong Chen and Brad R. Weiner  
XVI<sup>th</sup> International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.
3. *"Structure and Spectroscopic Properties of the Photofragment, ClSO Radical and Its Isomer, ClOS, in the Ground <sup>2</sup>A" State"*  
Gustavo E. Lopez, Brad R. Weiner and Yasuyuki Ishikawa  
XVI<sup>th</sup> International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.
2. *"Three Body Photodissociation of Thionyl Chloride"*  
Xirong Chen, Hongxin Wang and Brad R. Weiner  
1993 Conference on the Dynamics of Molecular Collisions, Helen, Georgia, 6-11 June 1993.
1. *"The Photochemistry of Thionylaniline"*  
K. Matos, X. Chen, H. Wang, and Brad R. Weiner  
205th National Meeting of the American Chemical Society, Denver, Colorado, 29 March - 2 April 1993.

#### Universities and National Laboratories (6)

6. *"Energy Disposal as a Probe of Chemical Reaction Mechanisms"* (invited)  
Brad R. Weiner  
Department of Chemistry, Emory University, Atlanta, Georgia, 20 October 1995
5. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)  
Brad R. Weiner  
Oak Ridge National Laboratories, Oak Ridge, Tennessee, 8 May 1995.
4. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)  
Brad R. Weiner  
Department of Chemistry, University of Houston, Houston, Texas, 25 April 1995.
3. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)  
Brad R. Weiner

Department of Chemistry, Marquette University, Milwaukee, Wisconsin, 10 November 1993

2. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)  
Brad R. Weiner  
Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 6 October 1993

1. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)  
Brad R. Weiner  
Department of Chemistry, Tulane University, New Orleans, Louisiana, 1 February 1993

**Regional (19)**

19. *"Study of the Energy Disposal into the Diatomic Photofragments Following the Gas Phase Photodissociation of Cyclic Sulfoxides"*  
Fei Wu, Xirong Chen, Yazmín Pedrogo and Brad R. Weiner  
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.

18. *"Excited State Dynamics of the Vinoxy Radical B State"*  
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner  
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.

17. *"Bimolecular Dynamics: Examining Sulfur Atom Transfer Reactions in A+BCD → AB+CD Systems"*  
Brad R. Weiner  
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.

16. *"Intramolecular Vibrational Energy Redistribution within Excited Electronic States of the Vinoxy Radical"*  
Ruolian Wan, Katherine I. Barnhard and Brad R. Weiner  
30th Annual Junior Technical Meeting, Ponce, Puerto Rico, 4 March 1995.

15. *"The Laser Photchemistry of Thionylaniline"*  
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner  
30th Annual Junior Technical Meeting, Ponce, Puerto Rico, 4 March 1995.

14. *"Laser Photodissociation of SO<sub>2</sub> at 193 and 210 nm"*  
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner  
Tropical Atmospheric Sciences Mini-Gordon Conference, Ponce, Puerto Rico, 24-25 February 1995

13. *"State-Resolved Fluorescence Lifetimes of the Vinoxy Radical: Evidence for Mode Selective Predissociation"*  
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner

Tropical Atmospheric Sciences Mini-Gordon Conference, Ponce, Puerto Rico, 24-25 February 1995

12. *"State-Resolved Distributions of Nascent  $SO(X^3\Sigma, v")$  following  $SO_2$  Photodissociation"*  
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner  
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
11. *"The Laser Photchemistry of Thionylaniline"*  
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner  
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
10. *"State-resolved Fluorescence Quenching of  $CH_2CHO(B)$ : Evidence for Mode-Selective Bond Scission"*  
Katherine L. Barnhard, Ruolian Wan and Brad R. Weiner  
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
9. *"Nascent  $SO(X^3\Sigma)$  Vibrational Distributions from the Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm"*  
Fei Wu, Xirong Chen and Brad R. Weiner  
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
8. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"*  
B.R. Weiner  
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
7. *"The Relaxation of Spin State Population of Nascent  $SO(X^3\Sigma)$  Following  $SO_2$  Photodissociation at 193 nm".*  
Ruolian Wan, Xirong Chen and Brad R. Weiner  
29th Annual Junior Technical Meeting, Mayagüez, Puerto Rico, 5 March 1994.
6. *"Nascent  $SO(X^3\Sigma)$  Vibrational Distributions from the Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm".*  
Fei Wu, Xirong Chen and Brad R. Weiner  
29th Annual Junior Technical Meeting, Mayagüez, Puerto Rico, 5 March 1994.
5. *"Nascent  $SO(X^3\Sigma)$  Vibrational, Rotational and Spin State Distributions from the 193 nm Photodissociation of  $SO_2$ "*  
Fei Wu, Xirong Chen, Yasuyuki Ishikawa and Brad R. Weiner  
17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993
4. *" $SO(X^3\Sigma)$  Production from the 193 nm Laser Photolysis of Thionyl Fluoride"*  
Hongxin Wang, Xirong Chen and Brad R. Weiner  
17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.
3. *"The Photochemistry of Thionylaniline"*

Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.

2. *"Multiphoton Ionization Spectrum of SOCl<sub>2</sub> in a Supersonic Jet"*

Manuel A. Rivera, T. Yabe and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

1. *"Vibrational Relaxation of Sulfur Monoxide Radicals at 298K"*

Félix M. Martínez, Xiaotian Gu and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

## VI. INTERACTIONS

Collaboration with Drs. H.H. Nelson and M. Hawley at the Chemistry Division, Naval Research Laboratory, Washington, D.C.

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**APPENDICES**